

Comment on "Correlated impurities and intrinsic spin liquid physics in the kagome material Herbertsmithite" (T. H. Han et al., Phys. Rev. B 94, 060409(R) (2016))

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Recently Han et al. [1] have provided an analysis of the observed behavior of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ Herbertsmithite based on a separation of the contributions to its thermodynamic properties due to impurities from those due to the kagome lattice. The authors developed an impurity model to account for the experimental data and claimed that it is compatible with the presence of a small spin gap in the kagome layers. We argue that the model they advocate is problematic, conflicting with the intrinsic properties of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ as observed and explained in recent experimental and theoretical investigations. We show that the existence of the gap in the kagome layers is not in itself of a vital importance, for it does not govern the thermodynamic and transport properties of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$. Measurements of heat transport in magnetic fields could clarify the quantum-critical features of spin-liquid physics of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$.

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In a frustrated magnet, spins are prevented from forming an ordered alignment, so they collapse into a liquid-like state named quantum spin liquid (QSL) even at the temperatures close to absolute zero. A challenge is to prepare quantum spin liquid materials in the laboratory and explain their properties. Han et al. have recently reported results from high-resolution low-energy inelastic neutron scattering on single-crystal $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ Herbertsmithite with the prospect of disentangling the effects on the observed properties of this material due to Cu impurity spins from the effects of the kagome lattice itself [1]. Citing single-crystal NMR and resonant X-ray diffraction measurements indicating that the impurities are 15% Cu on triangular Zn intercalates and the kagome planes are fully occupied with Cu, the authors assume that the corresponding impurity system may be represented as a simple cubic lattice in the dilute limit below the percolation threshold. They claim that this impurity model can describe the neutron-scattering measurements and specific heat data, and they suggest that it is compatible with the existence of a small spin-gap in the kagome layers [1–3]. Then, the model assumes that spin gap survives under the application of magnetic fields up to 9 T [2], while the bulk spin susceptibility χ exhibits a divergent Curie-like tail, indicating that some of the Cu spins act like weakly coupled impurities [1–3]. According to the impurity model, the divergent response seen in the dynamic spin susceptibility below 1 meV is due to the impurities [1, 2].

In this comment we show that 1) The proposed impurity model is artificial because it is inconsistent with the intrinsic properties of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ as observed and

described in recent experimental and theoretical studies of the behavior of its thermodynamic, dynamic and relaxation properties; 2) Explanation of these properties lies in the physics of the strongly correlated quantum spin liquid (SCQSL) present in this system, for the behavior of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ is in fact similar to that of heavy-fermion metals, with one main exception — $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ does not support an electrical current [4–12]; and 3) We demonstrate the proposed impurity model [1] cannot describe prior neutron, NMR, and specific heat data obtained in measurements in magnetic fields; it is also impossible to isolate the contributions coming from the impurities and the kagome planes. We conclude by recommending that measurements of heat transport in magnetic fields B be carried out; they could be crucial in revealing the mechanisms involved [7, 8, 11].

To examine the model of Han et al. in a broader context, we first refer to the experimental behavior of the thermodynamic properties of Herbertsmithite as summarized in Fig. 1. It is obvious from Fig. 1(a) that the magnetic susceptibility χ diverges in magnetic fields $B \leq 1$ T and that the Landau Fermi liquid (LFL) behavior is demonstrated at least for $B \geq 3$ T and low temperatures T ; at such temperatures and magnetic fields the impurities become fully polarized and hence do not contribute to χ [7, 11, 13]. Corresponding behavior follows from Fig. 1(b); it is seen that LFL behavior of the heat capacity C_{mag}/T emerges under application of the same fields. Consequently, we conclude that at $B \geq 3$ T and low T the contributions to both χ and C_{mag}/T from the impurities are negligible; rather, one could expect that they are dominated by the kagome lattice exhibiting a

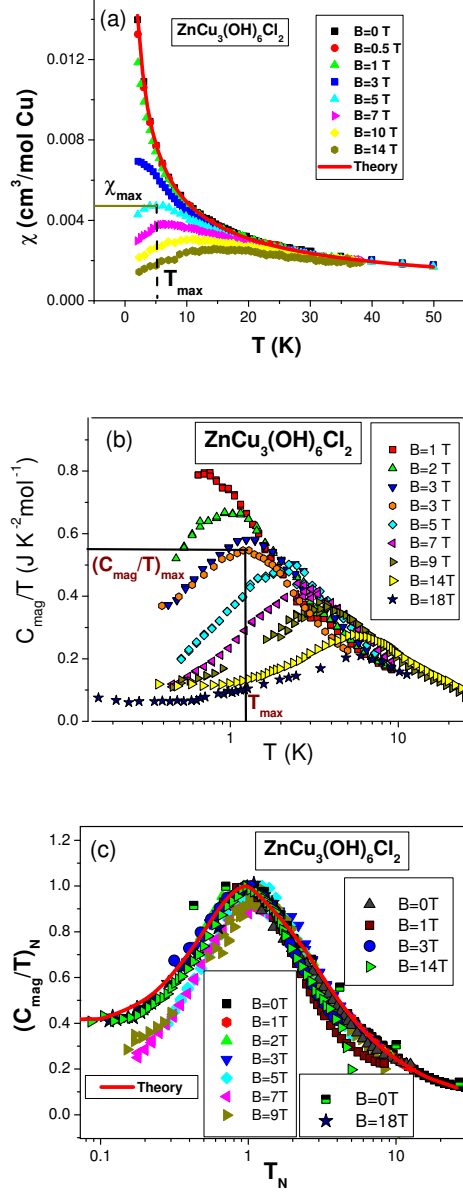


FIG. 1: Panel (a): Measured temperature dependence of the magnetic susceptibility χ of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ from Ref. [13] at magnetic fields shown in the legend. Illustrative values of χ_{max} and T_{max} at $B = 3$ T are also shown. A theoretical prediction at $B = 0$ is plotted as the solid curve, which represents $\chi(T) \propto T^{-\alpha}$ with $\alpha = 2/3$ [5, 11]. Panel (b): Specific heat C_{mag}/T measured on powder [14] and single-crystal [14–17] samples of Herbertsmithite, is displayed as a function of temperature T for fields B shown in the legend. Panel (c): Normalized specific heat $(C_{\text{mag}}/T)_N$ versus normalized temperature T_N as a function of B field values shown in the legend [9, 11]. The theoretical result from Ref. [5, 11], represented by the solid curve, traces the scaling behavior of the effective mass.

spin gap in the kagome layers [1–3]. Thus, one would expect both $\chi(T)$ and $C_{\text{mag}}(T)/T$ to approach zero for $T \rightarrow 0$ at $B \geq 3$ T. From panels (a)–(c) of Fig. 1, it is

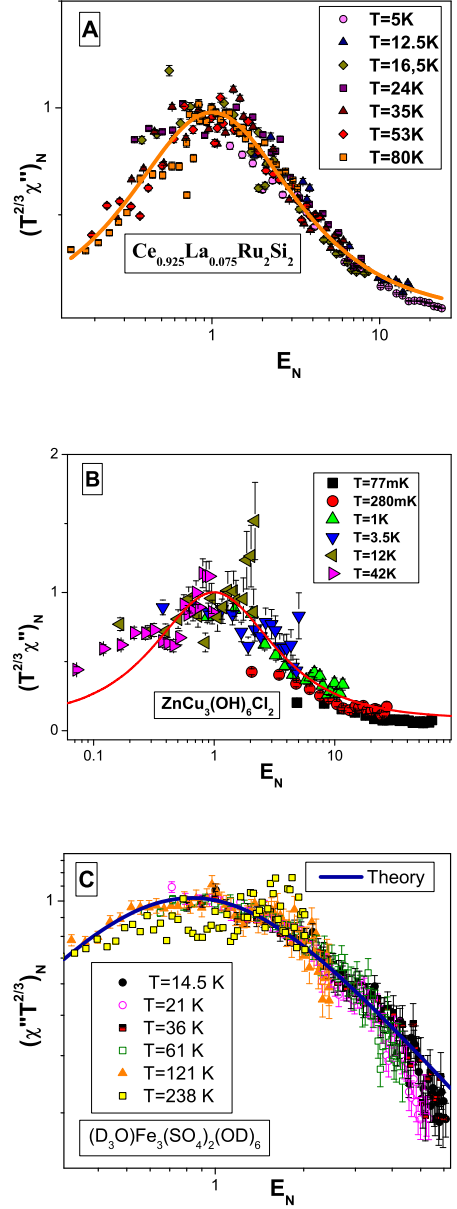


FIG. 2: Scaling behavior of the normalized dynamic spin susceptibility $(T^{2/3}\chi'')_N$ for three materials. Panel A: $(T^{2/3}\chi'')_N$ plotted against the dimensionless variable E_N . Data are extracted from measurements on the heavy-fermion metal $\text{Ce}_{0.925}\text{La}_{0.075}\text{Ru}_2\text{Si}_2$ [20]. Panel B: $(T^{2/3}\chi'')_N$ versus E_N . Data are extracted from measurements on Herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ [13]. Panel C: $(T^{2/3}\chi'')_N$ versus E_N . Data are extracted from measurements on the deuterium jarosite $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ [21]. Solid curve: Theoretical prediction based on Eq. (1). [6].

clearly seen that this is not the case, since for $B \geq 3$ T neither χ nor C_{mag}/T approach zero as $T \rightarrow 0$. Moreover, the normalized C_{mag}/T follows the uniform scaling

behavior displayed in Fig. 1(c), confirming the absence of a gap. It is also seen that the recent measurements of C_{mag} [14–17] are compatible with those obtained on powder samples. These observations support the conclusions that (i) the properties of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ under study are determined by a stable SCQSL, and (ii) an appreciable gap in the spectra of spinon excitations is absent even under the application of very high magnetic fields of 18 T. The latter conclusion is in accord with recent experimental findings that the low-temperature plateau in local susceptibility identifies the spin-liquid ground state as being gapless [18].

The same conclusions can be drawn from the neutron-scattering measurements of the dynamic spin susceptibility $\chi(\mathbf{q}, \omega, T) = \chi'(\mathbf{q}, \omega, T) + i\chi''(\mathbf{q}, \omega, T)$ as a function of momentum q , frequency ω , and temperature T . Indeed, these results play a crucial role in identifying the properties of the quasiparticle excitations involved. At low temperatures, such measurements reveal that relevant quasiparticles – of a new type insulator – are represented by spinons, form a continuum, and populate an approximately flat band crossing the Fermi level [19]. In such a situation it is expected that the dimensionless normalized susceptibility $(T^{2/3}\chi'')_N = T^{2/3}\chi''/(T^{2/3}\chi'')_{\text{max}}$ exhibits scaling as a function of the dimensionless energy variable $E_N = E/E_{\text{max}}$ [6, 11]. Specifically, the equation describing the normalized susceptibility $(T^{2/3}\chi'')_N$ reads [6, 11]

$$(T^{2/3}\chi'')_N \simeq \frac{b_1 E_N}{1 + b_2 E_N^2}, \quad (1)$$

where b_1 and b_2 are fitting parameters adjusted such that the function $(T^{2/3}\chi'')_N$ reaches its maximum value unity at $E_N = 1$ [6, 11]. Panel **A** of Fig. 2 displays $(T^{2/3}\chi'')_N$ values extracted from measurements of the inelastic neutron-scattering spectrum on the heavy-fermion (HF) metal $\text{Ce}_{0.925}\text{La}_{0.075}\text{Ru}_2\text{Si}_2$ [20]. The scaled data for this quantity, obtained from measurements on two quite different strongly correlated systems, $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ [13] and the deuterium jarosite $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ [21], are displayed in panels **B** and **C** respectively. It is seen that the theoretical results from Ref. [6] (solid curves) are in good agreement with the experimental data collected on all three compounds over almost three orders of magnitude of the scaled variable E_N and hence $(T^{2/3}\chi'')_N$ does exhibit the anticipated scaling behavior for these systems. From this observation we infer that the spin excitations in both $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ and $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$ demonstrate the same itinerant behavior as the electronic excitations of the HF metal $\text{Ce}_{0.925}\text{La}_{0.075}\text{Ru}_2\text{Si}_2$ and therefore form a continuum. This detection of a continuum is of great importance since it clearly signals the presence of a SCQSL in Herbertsmithite [6, 7, 11]. It is obvious from Fig. 2 that the calculations based on this premise are in good agreement with the experimental data, affirming the identification

of SCQSL as the agent of the low-temperature behavior of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ and $(\text{D}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OD})_6$. We can only conclude that the spin gap in the kagome layers is an artificial construction at variance with known properties of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$. In short, the demonstrable conflicts with experimental data we have identified negate the existence of a spin gap in the SCQL of Herbertsmithite. On the other hand, the existence of a gap in the kagome layers is not in itself of vital importance, for it does not govern the thermodynamic and transport properties of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$. Rather, these properties are determined by the underlying SCQSL. This assertion can be tested by measurements of the heat transport in magnetic fields, as has been done successfully in the case of the organic insulators [8, 22, 23]. Measurements of thermal transport are particularly salient in that they probe the low-lying elementary excitations of SCQSL in $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ and potentially reveal itinerant spin excitations that are mainly responsible for the heat transport. Surely, the overall heat transport is contaminated by the phonon contribution; however, this contribution is hardly affected by the magnetic field B . In essence, we expect that measurement of the B -dependence of thermal transport will be an important step toward resolving the nature of the SCQSL in $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ [7, 8, 11].

The SCQSL in Herbertsmithite behaves like the electron liquid in HF metals – provided the charge of an electron is set to zero. As a result, the thermal resistivity $w = L_T/\kappa$ of the SCQSL is given by [7, 8, 11]

$$w - w_0 = W_r T^2 \propto (M^*)^2 T^2, \quad (2)$$

where $W_r T^2$ represents the contribution of spinon-spinon scattering to thermal transport, being analogous to the contribution AT^2 to charge transport from electron-electron scattering. (Here L_T is the Lorenz number, κ the thermal conductivity, and w_0 the residual resistivity.) Based on this reasoning it follows that, under application of magnetic fields at fixed temperature, the coefficient W_r behaves like the spin-lattice relaxation rate shown in Fig. 3, i.e., $W_r \propto 1/(T_1 T)$, while in the LFL region at fixed magnetic field the thermal conductivity is a linear function of temperature, $\kappa \propto T$ [7, 8, 11].

Finally, we consider the effect of a magnetic field B on the spin-lattice relaxation rate $1/(T_1 T)$. From Fig. 3, which shows the normalized spin-lattice relaxation rate $1/(T_1 T)_N$ at fixed temperature versus magnetic field B , it is seen that increasing B progressively reduces $1/(T_1 T)$, and that as a function of B , there is an inflection point at some $B = B_{\text{inf}}$, marked by the arrow. To clarify the scaling behavior in this case, we normalize $1/(T_1 T)$ by its value at the inflection point, while the magnetic field is normalized by B_{inf} . Taking into account the relation $1/(T_1 T)_N \propto (M^*)^2$, we expect that a strongly correlated Fermi system located near its quantum critical point will exhibit the similar behavior of $1/(T_1 T)_N$ [4, 7, 8, 11]. Significantly, Fig. 3 shows that

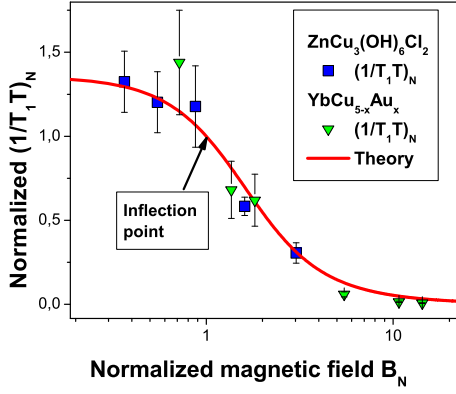


FIG. 3: Normalized spin-lattice relaxation rate $(1/T_1T)_N$ at fixed temperature as a function of magnetic field. Data for $(1/T_1T)_N$ extracted from measurements on $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ are shown by solid squares [24] and those extracted from measurements on $\text{YbCu}_{5-x}\text{Au}_x$ at $x = 0.4$, by the solid triangles [25]. The inflection point at which the normalization is taken is indicated by the arrow. The calculated result is depicted by the solid curve tracing the scaling behavior of $W_r \propto (M^*)^2$ (see Eq. (3)).

Herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ [24] and the HF metal $\text{YbCu}_{5-x}\text{Au}_x$ [25] do show the same behavior for the normalized spin-lattice relaxation rate. As seen from Fig. 3, for $B \leq B_{\text{inf}}$ (or $B_N \leq 1$) the normalized relaxation rate $1/(T_1T)_N$ depends weakly on the magnetic field, while it diminishes at the higher fields [4, 7, 8, 11] according to

$$W_r \propto 1/(T_1T)_N \propto (M^*)^2 \propto B^{-4/3}. \quad (3)$$

Thus, we conclude that the application of a magnetic field B leads to a crossover from NFL to LFL behavior and to a significant reduction in both the relaxation rate and the thermal resistivity.

In summary, we have demonstrated that both the impurity model of Herbertsmithite and the existence of a spin gap are problematic, as they contradict established properties of Herbertsmithite and are not supported by considerations of the thermodynamic and relaxation properties in magnetic fields. We conclude by recommending that measurements of heat transport in magnetic fields be carried out to clarify the quantum spin-liquid physics of Herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$.

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